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Overview of High-Temperature Superconductivity: Theory,  
Surfaces, Interfaces and Bulk Systems

by

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Physical Chemistry of High-Temperature Superconductors

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Interfaces and Bulk Systems

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An overview of the theoretical and experimental aspects of the recently-discovered superconducting compounds is presented. This overview is divided into three sections. In the first section a review of some of the theoretical and computational works is presented under the subsections entitled pairing mechanisms, electronic structure calculations and thermophysical properties. In the second section surface and interface chemistry issues related to the fabrication and use of high-temperature superconductors for high-performance applications are presented. Specific issues that are discussed include metallization and the formation of stable ohmic contacts, and chemically-stable overlayers that are suitable for passivation, protection and encapsulation of superconducting material structures that can then be used under a wide range of environmental conditions. Lastly, issues are discussed that are related to each of the bulk high-temperature superconducting ceramic oxides which have received so much attention the past two years. These include  $Tl_2Ba_2Ca_2Cu_3O_{10}$  with a critical temperature of 125 K, which is the current record.

## Theory

Since the discovery of high-temperature superconductivity in the CuO ceramics in the year 1986, there has been an explosion of theoretical works relating to these systems. It is not possible, in a short review of theoretical work like this, to examine the essential ideas of even a small fraction of this large body of literature. We select, quite arbitrarily, some of the work we are aware of and discuss the essential ideas of these. We apologize, in advance, to all the research workers whose work we have not reviewed.

This theoretical overview is divided into three sections: (1) pairing mechanism, (2) electronic structure calculations and finally, (3) thermophysical properties. In the section on pairing mechanism we review the basic microscopic mechanisms that might be responsible for producing superconducting states. This is a fundamental question and the success of any theoretical model addressing it should be judged in relation to the experiments it explains and the phenomena it predicts. The second part, dealing with electronic structure calculations, is quite important in that such calculations give detailed information about conduction processes, density of states and anisotropies in  $k$ -space. Finally, in the section on thermophysical properties we review works relating to phonon dispersion and soft modes, dynamics of tetragonal-to-orthorhombic phase transitions and the temperature and concentration dependence of the stability of these phases.

### (1) Pairing Mechanism:

In the conventional superconductors a pair of electrons of opposite spin and momentum form a bound state which leads to a coherent and highly correlated many-body superconducting state. The attractive interaction between the electrons of the pair is mediated by lattice vibrations (phonons) and the electrons overcome their strong Coulomb repulsion by staying away from each other in time (retardation). The basic question in the new superconductors is - What is the pairing mechanism? For a review of some of the early pairing models proposed for the high- $T_c$  materials we refer the reader to the work by Rice [1].

One of the leading theories for the high- $T_c$  superconductors is the resonating-valence-band (RVB) model proposed by Anderson [2] and his coworkers [3]. According to this model, the pairing mechanism is magnetic in origin and not of the conventional BCS type. The starting point of the RVB theory is a two-dimensional Hubbard model at half-filling with strong on-site Coulomb repulsion  $U$  and an attractive inter-site hopping energy  $t$ . Without oxygen doping (i.e., dopant concentration  $\delta = 0$ ), the ground state of the above model is expected to be a long-range anti-ferromagnetic (AF) state [4], but Anderson argues that frustration might favor a RVB state over an AF ground state. The basic idea of the RVB theory is that strong electron-electron correlations result in a separation of charge degrees of freedom from spin degrees of freedom. At low doping ( $\delta \neq 0$ ) and temperature, the quasi-particle excitations are believed to be "holons" (i.e., charge-carrying spinless particles) and "spinons" (i.e., spin- $\frac{1}{2}$  chargeless particles).

Superconductivity is due to formation of a condensate consisting of holon pairs. Since Bose-Einstein condensation is not possible in a strictly two-dimensional system, the interplanar couplings are important in giving rise to superconductivity.

The RVB theory has been amplified or modified in several ways [5,6,7], the details of which we won't go into here. Rice and Wang [8] have proposed a model in which superconductivity is due to condensation of a pair of bosons which gives rise to quasi-particle excitation energies which are similar to those of RVB theory, but different from BCS theory. Rice and Wang, however, favor a phonon interaction which mediates the attraction between the boson pair in question. Coffey and Cox [9] have given a nice summary of the essential points of the RVB theory in Section II of their paper.

Another theory that has been proposed is the spin-bag mechanism of Schrieffer's group [10]. The starting point of their theory is the strong AF spin order in the neighborhood of the superconducting transition ( $T_c$ ) and two-dimensional spin-correlations over a length  $L$  ( $\sim 200 \text{ \AA}$ ) in the neighborhood of the Neel transition ( $T_N \gg T_c$ ). Doping creates extra holes in the system and these are assumed to be localized over a length  $l$  ( $\ll L$ ). The spin of the hole couples to the spin density of the AF background through an exchange interaction. Within a given domain a hole produces an effective potential well or bag in its vicinity in which the hole is self-consistently trapped. The pairing is due to an effective attractive interaction between two holes which overcomes the short range Coulomb repulsion.

The importance of spins in producing a superconducting state has also been emphasized in a model proposed by Emery [11]. He has proposed that oxygen doping in the 214-material creates holes at the oxygen sites and that there is a narrow band of oxygen holes which couple strongly to the local spin configuration of the Cu-sites. This strong coupling is responsible for an attractive interaction between the oxygen holes.

We mention in passing that other mechanisms such as plasmons [12] and excitons [13] have also been proposed as possible candidates for being the condensate of the superconducting state.

Recently doubts have been expressed about the importance of the magnetic origin of the pairing interaction. The bismuth superconductors [14,15] ( $\text{BaKBiO}_3$ ) which are closely related in structure to the earlier superconductors and which are free of copper provide counter examples [16] to the magnetic origin of superconductivity. Another counter example [16] is the 123-material in which Cu is substituted 100% by Ag bringing  $T_c$  down to 40 K. This has led some people to propose that local structure might play a role in producing a superconducting state. A recent double-well model [17] of oxygen motion indicates trends in this direction; it has been shown that a strong  $T$ -dependent electron-phonon coupling parameter could produce  $T_c \approx 100 \text{ K}$ .

## (2) Electronic Structure Calculations:

The electronic structure [18-25] of the undoped compounds is of immense interest in getting a clue to the origin of superconductivity. These parent compounds are  $\text{La}_2\text{CuO}_4$  (denoted by 214),  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (denoted by 123) and  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  (denoted by

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2212). The important question is: Why is the ground state of these compounds an antiferromagnetic (AF) insulator? The band structure calculations, so far performed within the local density approximation, give results which are in contrast to the experimental situation - they all produce a metallic ground state. The reason for this discrepancy is believed to be the strong electron correlations in the CuO planes which are not adequately taken into account in a band picture. It would be interesting to have electronic structure calculations which take these correlations into account. In this regard, spin-polarized band structure calculations are expected to yield improved results over conventional band structure calculations. However, the results [23-25] of spin-polarized band structure calculations do not seem to be definitive.

We would like to conclude this section by stating some of the important conclusions that have emerged from the band structure calculations. In these calculations [18,19] the importance of the two-dimensional nature of the CuO planes was emphasized. The copper  $d(x^2-y^2)$  orbitals and the neighboring oxygen  $p(x,y)$  orbitals interact to produce bonding  $\sigma$  and antibonding  $\sigma^*$  orbitals. Similar results [20-22] were also obtained for 123- and 2212-compounds. Another important result is that the antibonding band was positioned closer to the Fermi energy  $E_F$ . In the new 2212-compounds, a pair of slightly filled Bi 6p bands provide additional carriers in the Bi-O planes [21]. A remarkable feature in these compounds is the charge separation between the two Bi-O planes [22].

### (3) Thermophysical Properties:

In this brief discussion of the thermophysical properties of the high- $T_c$  oxide superconductors we restrict ourselves to theoretical investigations of the lattice dynamics of these systems. In particular, we review the work on phonon modes and oxygen vacancy ordering and their influence on the structural transitions of the 214 and 123 superconductors. Knowledge of the phonon spectrum and its dependence on the oxygen distribution may prove to be of prime importance in elucidating the mechanism of high- $T_c$  superconductivity. Several scenarios of how electron-phonon interactions can lead to high transition temperatures have been proposed including oxygen motion in double wells [17], interlayer coupling [26,27] and coupling to soft quasicyclic modes associated with underconstrained nearest-neighbor rearrangements [28].

There have been a limited number of theoretical investigations on phonon frequencies and eigenvectors of the  $La_{2-x}(Ba,Sr)_x CuO_4$  [29-31] and  $YBa_2 Cu_3 O_{7-x}$  [32-35] superconductors. Unscreened lattice dynamical models [30,35], yielding only the bare phonon frequencies, gave fair agreement with experimentally determined total phonon density of states, mean square atomic vibrational amplitudes and Debye temperatures. Weber [29] has shown that the effect of screening, spectrum renormalization, due to conduction electrons gives rise to large Kohn anomalies near the Brillouin-zone boundary involving oxygen breathing modes. It was pointed out by Chaplot [35] that an additional effect of renormalization is to hybridize the high-frequency modes, dominated by oxygen, with the medium-

frequency, heavier-nuclei modes thus making necessary an effective-mass description for the analysis of the isotope effect. Cohen, et al. [31] employing the potential-induced breathing model were able to predict the tetragonal-to-orthorhombic phase transition in  $\text{La}_2\text{CuO}_4$  as arising from an instability, softening, in the  $B_{2g}$  tilting mode of the  $I4/mmm$  tetragonal structure. The onset of this transition has been recently derived from symmetry principles.

As is now well established,  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  undergoes a tetragonal-to-orthorhombic phase transition for  $1 > \delta > 0$  which is a consequence of oxygen vacancy ordering in the Cu-O basal plane. Several approaches have been undertaken to model this transition and describe the phase diagram in  $(T, \delta)$ -space. Most treatments are of the 2-D lattice gas type, employing first and second nearest-neighbor interactions for oxygen and vacancies and solved by mean field techniques [37-45]. Another approach, which has been successful in predicting the microstructure of the multiphase region, utilizes the method of concentration waves [46]; here the oxide is treated as an interstitial compound of ordered oxygen atoms and vacancies on a simple lattice [47]. The model of Mattis [48] deserves mention since it specifically accounts for the copper-oxygen bonds and thus enables predictions to be made concerning the dielectric response of the various phases. The picture that emerges from these studies is that at high temperatures,  $T > 750$  K, and/or stoichiometries  $\delta < 0.5$  a tetragonal phase exists with random ordering of oxygen and vacancies in the Cu-O basal plane. For material with  $\delta = 0$  the superconducting orthorhombic phase is stable with oxygen (atoms) and vacancies forming alternate chains along the crystal b-direction. At low temperatures and intermediate stoichiometries phase separation occurs with micro regions of tetragonal phase, orthorhombic phase and a second cell-doubled orthorhombic phase [45]. Phase transitions between the tetragonal and orthorhombic phases are of a second-order disorder-order type.

As a final note we mention the work on establishing the temperature domain in which thermal fluctuations and critical behavior dominate. Many of the theories described in this review are based on mean field techniques which become invalid when fluctuations are important. Estimates of the critical region, Ginzburg criterion, are in the range  $\xi^G \equiv (T_c - T)/T_c \sim 0.1 - 0.7$  [49-51]. However, it has been pointed out that the breakdown of mean-field behavior is progressive [51]; the ability of mean-field theory to predict non-universal quantities (prefactors, GL-parameters and  $T_c$ ) is lost within a region  $\xi^B \sim (\xi^G)^2$ , Brout criterion [52], which may cover most of the superconducting regime.

### Surfaces and Interfaces

The full integration of bulk and thin film high-temperature superconductors into existing and new technologies of high commercial value appears limited by a number of surface and interface materials issues. Many of these issues can be stated in general terms because they are shared by each type of ceramic superconductor (2-1-4, 1-2-3, or 2-1-2-2). Others are more specific to the material under study, e.g., the toxic character of the Tl 2-1-2-2 compound. As new materials with even higher critical temperatures are developed, analogous problems will be encountered.

Hence, the knowledge base developed for one class of ceramic material may also apply to others.

First, there are issues related to materials synthesis so that structures can be fabricated with predetermined shapes, sizes, and current carrying ability. These range from macroscopic to microscopic. Second, there are challenges related to the fabrication of superconducting thin films on a variety of substrates, with Si being an obvious choice from the perspective of microelectronic devices. Third, there are issues related to the formation of stable ohmic contacts, particularly for small samples and thin films. Fourth, there are problems related to the passivation, protection or encapsulation of small structures such as fibers or thin films, so that the superconducting oxides can be used under a wide range of environments. These and a great many other issues raise challenging chemical questions. Spectacular progress has been made in the few months that the new superconductors have been in existence, and we can anticipate that rapid progress will be made in the near future. These efforts that address fundamental issues will bring us one step closer to realizing breakthroughs in technologies of high commercial value.

It might be thought that surface and interface issues should be separated from those involved in the synthesis of the superconductors themselves. This is certainly not the case, however, because many of the most exciting opportunities for these materials will be in high performance applications. In these applications, the size of the superconducting elements will be comparable to those of the other components. Scaling down or shrinking the size of a structure exacerbates problems related to interfacial phenomena. Indeed, the challenges of forming, contacting, and protecting a superconducting strip 1  $\mu\text{m}$  wide and 0.1  $\mu\text{m}$  thick point to the intermingling of a wide range of materials issues.

To date, issues related to bulk synthesis and surface or interface characterization have also been intimately tied. This can be seen by noting that the starting point for surface or interface research is a well-characterized bulk material. Unfortunately for the surface scientist, early samples did not spring completely characterized from the firing furnaces, to paraphrase the springing-forth of Minerva completely armed from the head of Jupiter. Instead, early samples were sintered, were 70-90% dense, and individual grains were clad with other phases [53,54]. Difficulties in characterizing these interfaces and identifying their intrinsic properties are reflected in the literature of the last year for the 1-2-3 and 2-1-4 materials, and the last few months for the 2-1-2-2 materials. Only recently have bulk samples of sufficient quality been available so that fracturing could provide a clean surface [53]. Today, it is relatively routine to find single crystals having dimensions of greater than 1 mm, and several small companies are preparing to sell single crystals as large as 1 cm  $\times$  1 cm so that full characterization can be achieved.

Early studies indicated that polycrystalline, sintered samples of the 1-2-3 and 2-1-4 materials degraded rapidly upon exposure to a range of environments, including  $\text{H}_2\text{O}$ , CO,  $\text{CO}_2$ ,  $\text{O}_2$ , and solvents [55-57]. More recent work suggests that degradation is much slower and that some of the early problems were related to the intergranular



phases (e.g. carbonates or cuprates). Early work also showed that exposure of the 1-2-3's to high-intensity ultraviolet and X-ray photon beams produces substantial changes in the surfaces [58]. Again, recent work has indicated that most of the changes are related to the presence of second phases and were not intrinsic to the superconductors. At the same time, studies by Rosenberg and coworkers [59] pointed out some of the details of photon stimulated desorption. Electron beams of high current or high energy also induce damage. Exposure of these materials to energetic ions, such as used in Ar sputtering, leads to surface modification, structural changes, and the loss of superconductivity [53]. This damage points to the fragile character of these superconductors but also indicates that it may be possible to selectively alter portions of a thin film, for example writing nonsuperconducting lines on a superconducting template.

An issue that has arisen repeatedly has been the possibility of oxygen loss through the surface at room temperature. To our knowledge, there is no clear evidence that oxygen is lost under static vacuum conditions. Instead, the exposure of freshly prepared surfaces to ultrahigh vacuum leads to the chemisorption of residual gases from the vacuum system. Recent work with single crystals has provided evidence for the rearrangement of surface atoms after cleaving in vacuum [60]. This has been attributed to transgranular fracture and the exposure of energetically unfavorable surfaces. Indeed, such effects can be understood in terms of the highly anisotropic unit cell, but the restructuring does not necessarily result in oxygen loss.

Attempts to form contacts to surfaces or to investigate the electrical properties of the high-temperature superconductors have often been complicated by nonreproducibility. This can be related to the chemical processes that occur at these surfaces. As detailed studies of representative interfaces have shown, there is a strong tendency for reactive metals to leach oxygen from the superconductor to form new metal oxide bonding configurations [53,61]. The result of this interfacial chemistry is a heterogeneous transition region between the buried superconductor and the metal film. In particular, a cross section through an interface based on the 1-2-3, 2-1-4 or 2-1-2-2 superconductors would show the superconductor; a region where oxygen has been removed, where the structure is likely to be disrupted, and which is not superconducting; a region where the metal adatoms have formed electrically-resistive oxides; and the metal overlayer, possibly containing oxygen and dissociated superconductor atoms in solution and at the surface. Such an interface is shown schematically in Fig. 1. These interfaces are metastable because thermal processing will enhance oxygen transport to the metal layer and will increase the amount of substrate disruption. Certainly, these interfaces would not form the ohmic contacts desired in device applications. Likewise, the cladding of superconducting filaments with copper sheaths does not seem propitious since there will be interfacial interactions and the formation of a nonsuperconducting layer. The scale of this disrupted region is at least 50 Å for room temperature metal deposition and is likely to be much larger if the interface is processed at a higher temperature.

Ohmic contacts to these superconductors can be formed with Ag and Au overlayers [62]. These metals show minimal tendency to form oxides, and their deposition does not seriously disrupt the superconductor. For contacts, then, these metals appear to be the materials of choice. Two caveats should be noted, however. First, processing may lead to Au clustering, as has been observed for Au layers on many substrates. Second, if the surface to be metallized has been exposed to the air, it will be coated with hydrocarbons, water vapor and the like, and its superconducting properties will most likely be compromised. Attempts using Ar-ion sputtering to remove these contaminants prior to metallization have been successful, but almost certainly at the expense of the structural integrity of the surface. It remains to be seen whether the amount of surface damage (and loss of superconductivity) compromises the effective use of this approach to the fabrication of ohmic contacts for devices.

The protection of these superconductors is also crucial if they are to be integrated with other technologies. Much less is known about such passivation issues, although attempts are presently under way to develop protective overlayers. Two types of materials that have been examined so far and appear promising are metal oxides and non-metallic insulators [63]. Metal oxides have been formed by the deposition of metal atoms in an activated oxygen atmosphere to form a metal oxide precursor that does not leach oxygen from the substrate. The oxide layer then serves as a diffusion barrier against oxygen loss or atomic intermixing. To date, efforts have been successful with the oxides of Al and Bi, and it is likely that other oxides will prove to be effective as passivation layers and/or diffusion barriers. Those investigated so far are insulators, but future work may lead to conducting oxides that can serve as both contacts and passivators.

The second type of material that shows promise for passivation and electrical isolation is  $\text{CaF}_2$  [63]. This large-bandgap ionic insulator has a high static dielectric constant, can be readily evaporated from thermal sources in molecular form, and shows no tendency to modify the superconductor. As such, it may be useful as a dielectric layer in advanced devices.

We also note that both organic and inorganic polymers may be useful as encapsulants. In fact, fully protective coatings for high temperature superconductors may need to be developed to meet the specific demands of large- and small-scale applications. These protective coatings will likely involve a multilayer structure that would consist of thin- or thick-films of metals, low dielectric ceramics, and possibly organic and inorganic polymeric films. These multifunctional coatings would be effective as a diffusion barrier, would withstand environmental stress and temperature cycling, and would maintain strong adhesion. Specific opportunities exist for the synthesis of precursor molecules, such as organometallics, for chemical vapor deposition (CVD), or sol/gel approaches for low temperature fabrication of these multilayer protective coatings.

#### Bulk Superconducting Ceramic Oxides

Superconducting oxides have been known since 1964, but until recently the intermetallic compounds showed higher superconducting

temperatures. In 1975 research scientists at E. I. DuPont de Nemours [64] discovered superconductivity in the system  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$  with a  $T_c$  of 13 K. The structure for the superconducting compositions in this system is only slightly distorted from the ideal cubic perovskite structure. It is generally accepted that a disproportionation of the  $\text{Bi(IV)}$  occurs, namely,  $2\text{Bi(IV)}(6s^1) \rightarrow \text{Bi(III)}(6s^2) + \text{Bi(V)}(6s^0)$  at approximately 30 percent Bi. Sleight found that the best superconductors were single phases prepared by quenching from a rather restricted single-phase region, and hence these phases are actually metastable materials. At equilibrium conditions, two phases with different values of  $x$  would exist; the phase with a lower value of  $x$  would be metallic and with a higher value of  $x$  would be a semiconductor. It is important to keep in mind that the actual assignment of formal valence states is a convenient way of electron accounting; the actual states include appreciable admixing of anion functions. The system  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$  should be studied further since it contains compositions showing the highest  $T_c$  for any superconductor not containing a transition element. Recently, for example, Cava and Batlogg [14] have shown that  $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$  gave a  $T_c$  of almost 30 K, which is considerably higher than the 13 K reported for  $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$ .

$\text{La}_2\text{CuO}_4$  was reported by Longo and Raccan [65] to show an orthorhombic distortion of the  $\text{K}_2\text{NiF}_4$  structure with  $a = 5.363 \text{ \AA}$ ,  $b = 5.409 \text{ \AA}$  and  $c = 13.17 \text{ \AA}$ . It was also reported [66,67] that  $\text{La}_2\text{CuO}_4$  has a variable concentration of anion vacancies which may be represented as  $\text{La}_2\text{CuO}_{4-x}$ . Superconductivity has been reported for some preparations of  $\text{La}_2\text{CuO}_{4-x}$ . However, there appears to be some question as to the stoichiometry of these products since only a small portion of the material seems to exhibit superconductivity [68].

The extent of the anion vacancies has been recently reexamined [69], and the magnitude of this deficiency is less than can be unambiguously ascertained by direct thermogravimetric analysis which has a limit of accuracy in  $x$  of 0.01 for the composition  $\text{La}_2\text{CuO}_{4-x}$ . However, significant shifts in the Néel temperatures confirm a small variation in anion vacancy concentrations.

In the  $\text{La}_{2-x}\text{A}_x\text{CuO}_4$  phases ( $A = \text{Ca, Sr, Ba}$ ) the substitution of the alkaline earth  $x$  cation for the rare earth depresses the tetragonal-to-orthorhombic transition temperature. The transition disappears completely at  $x > 0.2$ , which is about the composition for which superconductivity is no longer observed. Compositions of  $\text{La}_{2-x}\text{A}_x\text{CuO}_4$  can also be prepared [70,71] where  $A$  is  $\text{Cd(II)}$  or  $\text{Pb(II)}$ . However, these phases are not superconducting, and it appears that the more basic divalent cations are necessary to allow  $\text{Cu(III)}$  to coexist with  $\text{O}^{2-}$ . The existence of  $\text{Cu(I)}$  and  $\text{Cu(III)}$  in  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$  is consistent with the ESR spectra, which shows the absence of square planar  $\text{Cu(II)}$ , and the Pauli-paramagnetic behavior over the temperature range from 77 to 300 K. Since the Pauli-paramagnetic behavior of  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$  is consistent with delocalized electrons, this would also indicate a high probability for the existence of  $\text{Cu(I)-Cu(III)}$  formed as a result of disproportionation of  $\text{Cu(II)}$  [72]. Subramanian et al. [73] have recently substituted both sodium and potassium into  $\text{La}_2\text{CuO}_4$ , giving rise to the compositions  $\text{La}_{2-x}\text{A}_x\text{CuO}_4$  ( $A = \text{Na, K}$ ). However, only the sodium substituted samples exhibited superconducting behavior.

The compound  $\text{Ba}_2\text{YCu}_3\text{O}_7$  shows a superconducting transition of  $\sim 93$  K and crystallizes as a defect perovskite. The unit cell of  $\text{Ba}_2\text{YCu}_3\text{O}_7$  is orthorhombic (Pmmm) with  $a = 3.8198(1)$  Å,  $b = 3.8849(1)$  Å and  $c = 11.6762(3)$  Å. The structure may be considered as an oxygen-deficient perovskite with tripled unit cells due to Ba-Y ordering along the c-axis. For  $\text{Ba}_2\text{YCu}_3\text{O}_7$ , the oxygens occupy 7/9 of the anion sites. One third of the copper is in 4-fold coordination and 2/3 are five-fold coordinated. A reversible structural transformation occurs with changing oxygen stoichiometry going from orthorhombic at  $x = 7.0$  to tetragonal at  $x = 6.0$  [74]. The value  $x = 7.0$  is achieved by annealing in oxygen at 400-500°C, and this composition shows the sharpest superconducting transition. It was shown by Davison et al. [72] that these materials are readily attacked by water and carbon dioxide in air to produce carbonates.

Recently Maeda et al. [75] reported that a superconducting transition of 120 K was obtained in the Bi/Sr/Ca/Cu/O system. The structure was determined for the composition  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  by several laboratories [76-78].

In most of the studies reported to date on the Bi/Sr/Ca/Cu/O system measurements were made on single crystals selected from multiphase products. The group at DuPont selected platy crystals having the composition  $\text{Bi}_2\text{Sr}_{3-x}\text{CaCu}_2\text{O}_{8+y}$  ( $0.9 > x > 0.4$ ) which showed a  $T_c \sim 95$  K. Crystals of  $\text{Bi}_2\text{Sr}_{3-x}\text{CaCu}_2\text{O}_{8+y}$  for  $x = 0.5$  gave orthorhombic cell constants  $a = 5.399$  Å,  $b = 5.414$  Å,  $c = 30.904$  Å [76]. These cell dimensions are consistent with the results of other investigators [77,78]. The structure consists of pairs of  $\text{CuO}_2$  sheets interleaved by Ca(Sr), alternating with double bismuth-oxide layers. Sunshine et al. [78] have indicated that the addition of Pb to this system raises the  $T_c$  above 100 K. There are now three groups of superconducting oxides which contain the mixed Cu(II)-Cu(III) oxidation states, namely  $\text{La}_{2-x}\text{A}_{1+x}\text{CuO}_4$  where  $\text{A}^{\text{II}} = \text{Ba, Sr, Ca}$ ;  $\text{RBa}_2\text{Cu}_3\text{O}_7$  where R is almost any lanthanide; and  $\text{Bi}_2\text{Sr}_{3-x}\text{CaCu}_2\text{O}_{8+y}$ .

Sheng and Herman have recently reported [79] on a high-temperature superconducting phase in the system Tl/Ba/Ca/Cu/O. Two phases were identified by Hazen et al. [80], namely  $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_9$  and  $\text{Tl}_2\text{Ba}_2\text{CaCu}_3\text{O}_{10}$ . Sleight et al. [76,81] have also reported on the structure of  $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$  as well as  $\text{Tl}_2\text{Ba}_2\text{CuO}_6$ . In addition, the superconductor  $\text{Tl}_2\text{Ba}_2\text{CaCu}_3\text{O}_{10}$  has been prepared by the DuPont group [82] and shows the highest  $T_c$  of any known bulk superconductor, namely  $\sim 125$  K.

A series of oxides with high  $T_c$  values has now been studied for the type  $(\text{A}^{\text{III}}\text{O})_2\text{A}^{\text{II}}\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2+2n}$ , where  $\text{A}^{\text{III}}$  is Bi or Tl,  $\text{A}^{\text{II}}$  is Ba or Sr, and  $n$  is the number of Cu-O sheets stacked. To date,  $n = 3$  is the maximum number of stacked Cu-O sheets examined consecutively. There appears to be a general trend whereby  $T_c$  increases as  $n$  increases. Unfortunately, these phases involve rather complex ordering, crystals of the phases are grown in sealed gold tubes, and excess reactants are always present. The toxicity as well as volatility of thallium, coupled with problems in obtaining reasonable quantities of homogeneous single-phase material, presents a challenge to the synthetic chemist. It will also be interesting to see if these materials are truly more stable over time than the  $\text{La}_{2-x}\text{A}_x\text{CuO}_4$  or  $\text{RBa}_2\text{Cu}_3\text{O}_7$  phases.

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Fig. 1 Schematic showing passivation of high-T<sub>c</sub> superconductor surface with Ag, Au, and composite materials (left) compared to disruptive reaction for chemically active overlayers (right).

# Overlayers/Contacts on Superconductors

**Passivation**

**Reaction**

metal  
superconductor

metal  
metal oxide  
disrupted substrate  
superconductor

extended  
interface

Ag, Au

$\text{Bi}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$

$\text{CaF}_2$

Ti, Fe, Cu, La

Al, In, Pd, Bi

Ge

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